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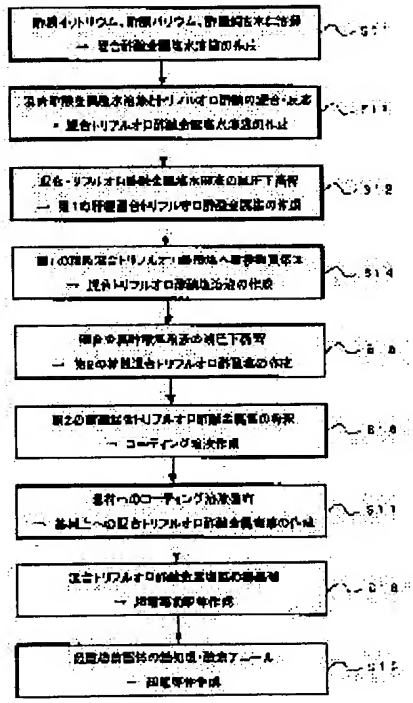
(54) METHOD OF MANUFACTURING OXIDE SUPERCONDUCTOR, RAW MATERIAL FOR OXIDE SUPERCONDUCTOR AND METHOD OF MANUFACTURING RAW MATERIAL FOR OXIDE SUPERCONDUCTOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method of a high-performance oxide superconductor wherein a metal acetate is utilized as a starting material.

SOLUTION: The oxide superconductor is manufactured by a mixing-reaction process wherein a mixed metal trifluoroacetate solution is prepared by mixing the mixed acetate aqueous solution which contains one or more metal elements selected from lanthanoids and yttrium, barium and copper with trifluoroacetic acid and reacting, and a refining process wherein a refined mixed metal trifluoroacetate is prepared from the mixed metal acetate solution by adjusting the total content of water and acetic acid component to ≤2 wt.%.



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CLAIMS

[Claim(s)]
[Claim 1] A manufacture method of oxides superconductors characterized by providing the following. Mixing / reaction production process which mix [trifluoroacetic acid and], and one or more kinds of metallic elements chosen from a lanthanoids group and an yttrium, barium, and a mixed acetate aqueous solution containing copper are made to react, and creates a mixed trifluoroacetic acid metal salt water solution A purification production process at which a sum total content of moisture and an acetic-acid component creates a purification mixing trifluoroacetic acid metal salt which is 2 or less % of the weight from a mixed trifluoroacetic acid metal salt water solution created by said mixing / reaction production process A dissolution production process which dissolves in a solvent a mixed trifluoroacetic acid metal salt created by said purification production process, and creates a coating solution A heat treatment process which applies to a base material a coating solution created by said dissolution production process, heat-treats a base material with which a film of a mixed trifluoroacetic acid metal salt was created by a membrane formation production process which creates a film of a mixed trifluoroacetic acid metal salt, and said membrane formation production process, and creates a superconductor
[Claim 2] A manufacture method of oxides superconductors according to claim 1 that said one or more kinds of metals are characterized by thing of an yttrium, neodium, samarium, a gadolinium, and an ytterbium included for either at least.
[Claim 3] Claim 1 said whose solvent is characterized by including a hydrocarbon compound of a liquid in temperature of 30 degrees C, and an atmospheric pressure of 1013hPa thru/or a manufacture method of oxides superconductors given in any 1 term of 2.
[Claim 4] A manufacture method of oxides superconductors according to claim 3 that said solvent is characterized by including either a methanol, ethanol, 1-propanol and 2-propanol.
[Claim 5] Claim 1 whose sum total content of moisture contained in said mixed trifluoroacetic acid metal salt and an acetic-acid component is characterized by being 0.5 or less % of the weight thru/or a manufacture method of oxides superconductors given in any 1 term of 4.
[Claim 6] A manufacture method of oxides superconductors of claim 1 thru/or an any 1 term publication of five characterized by providing the following. The 1st distillation process which creates the 1st purification trifluoroacetic acid metal salt to which said purification production process distilled under reduced pressure of mixed trifluoroacetic acid metal salting in liquid created by said mixing / reaction production process, and reduced moisture and acetic-acid components said 1st purification trifluoroacetic acid metal salt created by said 1st distillation process -- this -- an addition production process which adds replaceable material which can be replaced by moisture in the 1st purification trifluoroacetic acid metal salt, and acetic-acid component The 2nd distillation process which creates a purification trifluoroacetic acid metal salt of an account 2nd which distilled under reduced pressure of said 1st purification trifluoroacetic acid metal salt to which said replaceable material was added, and reduced moisture and acetic-acid components according to said addition production process
[Claim 7] A manufacture method of oxides superconductors claim 6 publication that said replaceable material is characterized by including a hydrocarbon compound of a liquid in temperature of 30 degrees

C, and an atmospheric pressure of 1013hPa.
[Claim 8] A manufacture method of oxides superconductors according to claim 7 that said replaceable material is characterized by including either a methanol, ethanol, 1-propanol and 2-propanol.
[Claim 9] Claim 1 some of [at least] whose surfaces of said base material are characterized by being formed from a material with which a grid mismatch with a superconductor has corrosion-proof nature to a steam and hydrogen fluoride within **7% thru/or a manufacture method of oxides superconductors given in any 1 term of 8.
[Claim 10] A manufacture method of oxides superconductors according to claim 9 characterized by forming some [at least] surfaces of said base material from either a magnesia of orientation which has LaAlO3 of orientation (100), and a surface layer of crystalline Seria (100), or (100) yttria stabilized zirconia of orientation.
[Claim 11] Claim 1 characterized by including a precursor creation production process that said heat treatment process decomposes a trifluoroacetic acid component, and creates a superconduction precursor, and a superconductor creation production process which creates oxides superconductors from said superconduction precursor created by said precursor creation production process thru/or a manufacture method of oxides superconductors given in any 1 term of 10.
[Claim 12] A manufacture method of oxides superconductors according to claim 11 characterized by including a production process at which said precursor creation production process heat-treats in a humidified pure oxygen ambient atmosphere.
[Claim 13] Claim 11 characterized by said superconductor creation production process including humidified oxygen and a production process at which it heat-treats in a mixed-gas ambient atmosphere of inert gas thru/or a manufacture method of oxides superconductors given in any 1 term of 12.
[Claim 14] A raw material for oxides superconductors characterized by being a raw material for oxides-superconductors manufacture containing one or more kinds of metals chosen from a metal and an yttrium of a lanthanoids group, barium, and a copper mixed trifluoroacetic acid metal salt, and a sum total content of moisture and an acetic-acid component being 0.5 or less % of the weight of a mixed trifluoroacetic acid metal salt.
[Claim 15] A manufacture method of a raw material for oxides superconductors characterized by providing the following. Mixing / reaction production process which mix [trifluoroacetic acid and], and an element of a lanthanoids group and an yttrium, barium, and an acetate aqueous solution containing one or more kinds of metallic elements chosen from copper are made to react, and creates trifluoroacetic acid metal salting in liquid The 1st distillation process which creates the 1st purification trifluoroacetic acid metal salt which distilled under reduced pressure of mixed trifluoroacetic acid metal salting in liquid created by said mixing / reaction production process, and reduced moisture and acetic-acid components said 1st purification trifluoroacetic acid metal salt created by said 1st distillation process -- this -- an addition production process which adds replaceable material which can be replaced by moisture in the 1st purification trifluoroacetic acid metal salt, and acetic-acid component The 2nd distillation process to which it distills under reduced pressure of said 1st purification trifluoroacetic acid metal salt to which said replaceable material was added, and a sum total content of moisture and an acetic-acid component creates 2 or less % of the weight of the 2nd purification trifluoroacetic acid metal salt according to said addition production process

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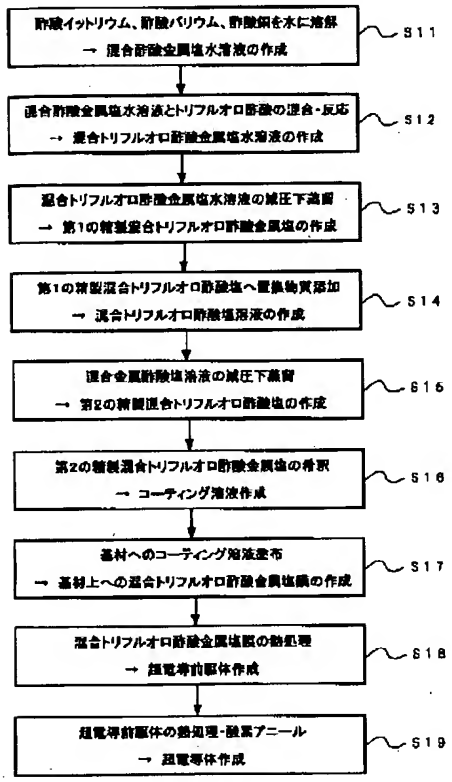
Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] Especially this invention relates to the manufacture method of the manufacture method of oxides superconductors using a trifluoroacetic acid metal salt, the raw material for oxides superconductors, and the raw material for oxides superconductors about the manufacture method of the manufacture method of oxides superconductors, the raw material for oxides superconductors, and the raw material for oxides superconductors.
[0002]
[Description of the Prior Art] As for oxides superconductors, the application to a superconduction coil, a superconduction magnet, a nuclear fusion reactor, a maglev train, an accelerator, magnetic diagnostic equipment (Magnetic Resonance Imaging etc.), superconduction magnetic energy are recording (Superconducting Magnetic Energy Storage), etc. is expected, and this part is already being put in practical use.
[0003] There is a superconductor of a bismuth system and an yttrium system in an oxide superconductivity object, and since it is hard to produce the fall of properties, such as critical current density, also under a magnetic field, the yttrium system superconductor attracts attention.
[0004] as the manufacture method of an yttrium system superconductor -- a pulse laser (Pulse Laser) -- law and liquid phase epitaxy deposition (Liquid Phase Epitaxy) -- law and an electron beam (Electron Beam) -- although there is law etc. -- organic metal deposition (Metal Organic Deposition) -- since law does not need a vacuum but can manufacture oxide superconductivity by low cost, it attracts attention. and the trifluoroacetic acid-organic metal deposition (Tri-Fluoroacetic Acid Metal Organic Deposition) which used the trifluoroacetic acid of a fluorine compound also in the organic metal depositing method -- possibilities attract attention to law (henceforth the "TFA-MOD method") from the simple nature.
[0005] As a TFA-MOD method, the method of using metal acetate and water as a start raw material is tried by Gupta (bibliography: A.Gupta, et al, Appl.Phys.Lett.vol.52 (No.24), page2077 (1988)) or McIntyre, Cima (bibliography-.C.McIntyre, et al, Appl.Phys.vol.68 (No.8), page4183 (1990)), etc.
[0006]
[Problem(s) to be Solved by the Invention] However, it was difficult to manufacture the oxides superconductors which have a property high as a start raw material for metal acetate and water. Consequently, the report that the superconductor which has the critical current density which exceeds 1 MA/cm2 by 0.1 micrometers or more of thickness by this method was manufactured is not performed.
[0007] what was made in order that this invention might solve such a technical problem -- it is -- metal acetate -- as a start raw material -- available -- in addition -- and it aims at offering the method of manufacturing the oxides superconductors which have a high property.
[0008]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, (1) A manufacture method of oxides superconductors of this invention One or more kinds of metallic elements chosen from a lanthanoids group and an yttrium, Mixing / reaction production process which mix [trifluoroacetic

acid and], and barium and a mixed acetate aqueous solution containing copper are made to react, and creates a mixed trifluoroacetic acid metal salt water solution, A purification production process at which a sum total content of moisture and an acetic-acid component creates a purification mixing trifluoroacetic acid metal salt which is 2 or less % of the weight from a mixed trifluoroacetic acid metal salt water solution created by said mixing / reaction production process, A dissolution production process which dissolves in a solvent a mixed trifluoroacetic acid metal salt created by said purification production process, and creates a coating solution, A membrane formation production process which applies to a base material a coating solution created by said dissolution production process, and creates a film of a mixed trifluoroacetic acid metal salt, It is characterized by providing a heat treatment process which heat-treats a base material with which a film of a mixed trifluoroacetic acid metal salt was created, and creates a superconductor according to said membrane formation production process.

[0009] A sum total content of moisture and an acetic-acid component can create oxides superconductors of a property excellent in creating a purification mixing trifluoroacetic acid metal salt which is 2 or less % of the weight.

[0010] Said purification production process distills mixed trifluoroacetic acid metal salting in liquid created by said mixing / reaction production process under reduced pressure here. The 1st distillation process which creates the 1st purification trifluoroacetic acid metal salt which reduced moisture and acetic-acid components, said 1st purification trifluoroacetic acid metal salt created by said 1st distillation process -- this -- with an addition production process which adds replaceable material which can be replaced by moisture in the 1st purification trifluoroacetic acid metal salt, and acetic-acid component It can distill under reduced pressure of said 1st purification trifluoroacetic acid metal salt to which said replaceable material was added according to said addition production process, and the 2nd distillation process which creates a purification trifluoroacetic acid metal salt of the account 2nd which reduced moisture and acetic-acid components can be provided.

[0011] Replaceable material which can be replaced by moisture in the 1st purification trifluoroacetic acid metal salt and acetic-acid component is added, and, as for the 2nd purification trifluoroacetic acid metal salt created by distilling under reduced pressure, many of moisture in the 1st purification trifluoroacetic acid metal salt and acetic-acid components are replaced by replaceable material. Consequently, a sum total content of moisture in the 2nd purification trifluoroacetic acid metal salt and an acetic-acid component is reduced compared with the 1st purification trifluoroacetic acid metal salt. Creation of a superconductor of a property excellent in using this 2nd purification trifluoroacetic acid metal salt is attained.

[0012] (2) A raw material for oxides superconductors concerning this invention is a raw material for oxides-superconductors manufacture containing one or more kinds of metals chosen from a metal and an yttrium of a lanthanoids group, barium, and a copper mixed trifluoroacetic acid metal salt, and a sum total content of moisture and an acetic-acid component is characterized by being 0.5 or less % of the weight of a mixed trifluoroacetic acid metal salt.

[0013] This raw material for oxides superconductors can be used as a raw material for creating oxides superconductors of Y123 system by mixing with a suitable mixing ratio if needed. And creation of extremely excellent oxides superconductors of a property of a sum total content of moisture and an acetic-acid component is attained from it being 0.5 or less % of the weight at this raw material.

[0014] (3) A manufacture method of a raw material for oxides superconductors concerning this invention Mixing / reaction production process which mix [trifluoroacetic acid and], and an acetate aqueous solution containing a metal of a lanthanoids group and an yttrium, barium, and one or more kinds of metals chosen from copper is made to react, and creates trifluoroacetic acid metal salting in liquid, Mixed trifluoroacetic acid metal salting in liquid created by said mixing / reaction production process is distilled under reduced pressure. The 1st distillation process which creates the 1st purification trifluoroacetic acid metal salt which reduced moisture and acetic-acid components, said 1st purification trifluoroacetic acid metal salt created by said 1st distillation process -- this -- with an addition production process which adds replaceable material which can be replaced by moisture in the 1st purification trifluoroacetic acid metal salt, and acetic-acid component It is characterized by providing the 2nd

distillation process to which it distills under reduced pressure of said 1st purification trifluoroacetic acid metal salt to which said replaceable material was added, and a sum total content of moisture and an acetic-acid component creates 2 or less % of the weight of the 2nd purification trifluoroacetic acid metal salt according to said addition production process.
[0015] With the 1st distillation process and an addition production process, and the 2nd distillation process, a sum total content of moisture and an acetic-acid component can create 2 or less % of the weight of the 2nd purification trifluoroacetic acid metal salt, and this 2nd purification trifluoroacetic acid metal salt can be used as a raw material for mixing for creating a superconductor of an outstanding property.
[0016]
[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to details with reference to a drawing.
(1st operation gestalt) Drawing 1 is flow drawing showing the production process of the manufacture method of the oxides superconductors concerning the gestalt of operation of the 1st of this invention. The manufacture method of the oxides superconductors built over this invention as shown in drawing 1 is expressed with the production process of S11 to S19.
[0017] (1) Dissolve one or more kinds of metallic elements chosen from the lanthanoids group and the yttrium (Y), barium, and the acetate containing copper in water, and create mixed acetic-acid metal salting in liquid (S11).
[0018] Drawing 1 shows the example which used the yttrium (Y) as "one or more kinds of metallic elements chosen from the lanthanoids group and the yttrium." Also in the production process of the following steps S12-S19, all "yttriums" shall express the example of representation of "one or more kinds of metallic elements chosen from the lanthanoids group and the yttrium."
[0019] A "lanthanoids group" says the metallic element group from the lanthanum of an atomic number 57 to the lutetium of an atomic number 71, for example, neodium (Nd), samarium (Sm), a gadolinium (Gd), and an ytterbium (Yb) are contained. It follows, the mixture of samarium (Sm), samarium, and an yttrium is contained as "one or more kinds of metals chosen from the metal and yttrium of a lanthanoids group", and it gets.
[0020] Respectively, the acetate of these "one or more kinds of metallic elements", barium, and copper is desirable, when mixing so that it may be set to 1:2:3 by the mole ratio of a metal ion creates the oxides superconductors of a good property. This is based on the crystal structure of the so-called oxides superconductors (for example, Ba2YCu 3O7) of Y123 system. However, the gap from [some of] this ratio is permitted, and it deals in it.
[0021] It is desirable to use the pure water created for example, by the ion-exchange method etc. as "water", when preventing mixing of an impurity.
[0022] thus, yttrium acetate (Y(OCOCH3) 3), barium acetate (Ba2 (OCOCH3)), and copper acetate (Cu2 (OCOCH3)) -- the aqueous solution of the mixed acetic-acid metal salt in which the ion of Y, Ba, and Cu is contained at about 1:2:3 rate by the mole ratio can be created by dissolving the powder of each hydrate in pure water.
[0023] (2) Mix [trifluoroacetic acid (CF3COOH) and], make a mixed acetate aqueous solution react, and create a mixed trifluoroacetic acid metal salt water solution (S12).
[0024] As a result of mixing a solution, the solution of a mixed trifluoroacetic acid metal salt with which the ion of "one or more kinds of metallic elements", barium (yttrium etc.), and copper reacts with trifluoroacetic acid, for example, a trifluoroacetic acid yttrium (CF3COO) (3Y), trifluoroacetic acid barium (CF3COO) (2Ba), and trifluoroacetic acid copper (CF3COO) (2Cu) are contained is created.
[0025] As for the amount of mixing of the trifluoroacetic acid at this time, it is desirable to consider as mixed acetate and a reaction equimolecular amount (for it to react an equimolecular amount every and for too much molecule not to arise) so that all the acetic-acid radicals of mixed acetate may replace a trifluoroacetic acid radical.
[0026] (3) Distill under reduced pressure of a mixed trifluoroacetic acid metal salt water solution, and create the 1st purification trifluoroacetic acid metal salt (S13).

[0027] For example, moisture and an acetic-acid component are distilled from mixed trifluoroacetic acid metal salting in liquid by heating decompressing the container into which the solution was put using the rotating evaporator etc. It is desirable when distilling rotating the container into which the solution was put here creates the 1st homogeneous purification trifluoroacetic acid metal salt.
[0028] the moisture which remains adjusting a pressure and temperature suitably at the time of distillation, and preventing bumping at it -- and it is made to decrease as long as it can carry out an acetic-acid component For example, in early stages of distillation, a pressure is made to 120hPa, temperature is made into 40 degrees C, and reduced pressure and a temperature up are gradually performed with reduction of moisture and an acetic-acid component. The distillation time amount at this time is about 8 hours. Consequently, translucent blue gel or the 1st sol-like purification mixing trifluoroacetic acid metal salt can be obtained. In this 1st purification mixing trifluoroacetic acid metal salt, the moisture and acetic-acid component which were not able to evaporate make it a sum total content, for example, are contained about 2 to 8% of the weight.
[0029] (4) Add the replaceable material which can be replaced by the acetic-acid component in the 1st purification trifluoroacetic acid metal salt to the 1st purification trifluoroacetic acid metal salt, and create a mixed trifluoroacetic acid solution (S14).
[0030] It is a sol or gel material, and trifluoroacetic acid metal salinity children, such as a trifluoroacetic acid yttrium, approach and exist by hydrogen bond etc., it joins together physically [a water molecule and an acetic-acid molecule] or in static electricity, and the mixed trifluoroacetic acid metal salt exists in the crevice. It is a difficult reason that this removes moisture and an acetic-acid component completely.
[0031] The oxides superconductors of a property excellent in removing moisture and an acetic-acid component from a mixed trifluoroacetic acid metal salt can be obtained. That is, it is hard coming to carry out membrane formation of the mixed trifluoroacetic acid metal salt to a base material top as removal of moisture being inadequate. Moreover, if an acetic-acid component remains, in order that carbon may remain in oxides superconductors to the creation time of oxides superconductors, it will become easy for critical current density to fall.
[0032] In order to remove moisture and an acetic-acid component, the replaceable material which can be replaced by the moisture in it and the acetic-acid component is added to the 1st purification trifluoroacetic acid metal salt. By carrying out the 2nd distillation process of the following step S15, this replaceable material replaces by the moisture in a purification trifluoroacetic acid metal salt, and the acetic-acid component, and the moisture and acetic-acid component in a trifluoroacetic acid metal salt are reduced.
[0033] It cannot react easily with a trifluoroacetic acid metal salt except that substitute with the moisture in a purification trifluoroacetic acid metal salt and an acetic-acid component is possible for this replaceable material, and it is necessary to have the property which cannot remain further easily in a superconductor to the creation time of a superconductor. Consequently, ordinary temperature and the low-grade hydrocarbon compound which has the hydroxyl group of a liquid condition by ordinary pressure (30 degrees C, 1013hPa), for example, a methanol, ethanol, 1-propanol, 2-propanol, etc. can be chosen as replaceable material.
[0034] It requires that it is lower alcohol because carbon becomes easy to remain in a superconduction precursor with a hydrocarbon compound with many carbon numbers when a superconduction precursor is created in the below-mentioned step S18. The residual of the carbon in a superconduction precursor, as a result a superconductor can become the cause which causes the fall of a superconduction property.
[0035] Enough, for example, the 50 to 200 times as much replaceable material which remained as the sum total weight of moisture and an acetic-acid component is added, and mixed trifluoroacetic acid salting in liquid is created than the sum total content of the moisture which remained this replaceable material in the mixed trifluoroacetic acid metal salt, and an acetic-acid component. Consequently, weight % of the sum total content of the moisture in this mixed trifluoroacetic acid salting in liquid and an acetic-acid component falls to 1 / 50 - 1/200 as compared with a mixed trifluoroacetic acid salt.
[0036] (5) Distill under reduced pressure of said 1st purification trifluoroacetic acid metal salting in

liquid with which replaceable material was added, and create the 2nd purification trifluoroacetic acid metal salt (S15).
[0037] For example, mixed trifluoroacetic acid metal salting in liquid is distilled by heating decompressing the container into which the solution was put using the rotating evaporator etc., and moisture and an acetic-acid component are removed.
[0038] The temperature at this time and a pressure control a pressure and temperature suitably according to replaceable material so that moisture and an acetic-acid component tend [as possible] to evaporate. For example, in using a methanol as replaceable material, it considers as the pressure of 240Pa, and the temperature of 35 degrees C in early stages of distillation, and performs reduced pressure and a temperature up gradually with evaporation of moisture and an acetic-acid component.
[0039] When a methanol is used as replaceable material, the boiling point is low compared with water or an acetic acid. For this reason, although more directions of a methanol than moisture and an acetic-acid component evaporate from mixed trifluoroacetic acid metal salting in liquid, evaporation of moisture or an acetic-acid component takes place with evaporation of a methanol. For this reason, the moisture and acetic-acid component in mixed trifluoroacetic acid metal salting in liquid decrease with distillation. It is desirable when making moisture distill creates the 2nd homogeneous purification trifluoroacetic acid metal salt, rotating the container into which the solution was put here.
[0040] As mentioned above, moisture and an acetic-acid component are removed from the 1st purification mixing trifluoroacetic acid as a result of steps S14 and S15, and the 2nd purification mixing trifluoroacetic acid metal salt is created.
[0041] It is the material of the shape of blue gel with this 2nd translucent purification mixing trifluoroacetic acid metal salt, or a sol, and the water molecule and the acetic-acid molecule exist in the molecule of replaceable material, such as a methanol, and the pan in the crevice between trifluoroacetic acid metal salinity children combined mutually.
[0042] However, with the 2nd purification mixing trifluoroacetic acid metal salt, since many of moisture contained in the 1st purification mixing trifluoroacetic acid metal salt and acetic-acid components are replaced with replaceable material, the content of moisture and an acetic-acid component is decreasing. For example, if the 90% replaces replaceable material noting that the sum total content of the moisture contained in the 1st purification mixing trifluoroacetic acid metal salt and an acetic-acid component is 8 % of the weight, the sum total content of the moisture in the 2nd purification mixing trifluoroacetic acid metal salt and an acetic-acid component will become 8x0.1=0.8 % of the weight.
[0043] Thus, it is possible to make the sum total content of the moisture of the 2nd purification mixing trifluoroacetic acid and an acetic-acid component into 2 or less % of the weight. Consequently, the creation of a superconductor which has a good property using this 2nd purification mixing trifluoroacetic acid is attained.
[0044] It becomes it is possible to replace moisture and an acetic-acid component by replaceable material with a rate better than 90% in fact, and possible to make the sum total content of the moisture in the 2nd purification mixing trifluoroacetic acid metal salt, and an acetic-acid component into less than 0.5 % of the weight.
[0045] (6) Dilute the 2nd purification mixing trifluoroacetic acid salt with a solvent, and create a coating solution (S16).
[0046] As a solvent, low-grade hydrocarbon compounds, such as the hydrocarbon compound of a liquid condition, for example, a methanol, ethanol, 1-propanol, and 2-propanol, can be used by ordinary temperature and ordinary pressure (30 degrees C, 1013hPa). It requires that it is a low-grade hydrocarbon compound because carbon becomes easy to remain in a superconduction precursor with a hydrocarbon compound with many carbon numbers when a superconduction precursor is created in the below-mentioned step S18. The residual of the carbon in a superconduction precursor, as a result a superconductor can become the cause which causes the fall of a superconduction property.
[0047] The degree of dilution is adjusted that a coating solution should be made suitable viscosity on the occasion of dilution. It is for creating mixed trifluoroacetic acid metal **** of predetermined thickness on a base material. That is, if you want for it to be large in viscosity if you want to thicken thickness,

and to make thickness thin, the amount of addition of a solvent will be adjusted so that viscosity may become low.

[0048] (7) Apply a coating solution to a base material and form the film of a mixed trifluoroacetic acid metal salt (S17).

[0049] It is desirable to be formed from the material which a grid mismatch with oxides superconductors is less than **7%, and some [at least] surfaces of a base material cannot corrode easily to a steam and hydrogen fluoride as a base material.

[0050] In order that the crystal structure of Y123 system may discover superconduction, it is required of oxides superconductors in this case. In order to follow and to perform crystal growth of Y123 structure on a base material, it will be desirable that this crystal structure and lattice matching are performed.

[0051] Moreover, since fluorides, such as hydrogen fluoride, are generated as a result of disassembly of a superconduction precursor in step S19 using a steam at the formation production process (steps S18 and S19) of the superconductor mentioned later, it will be desirable that it is the material which a base material cannot corrode easily due to fluorides, such as moisture and hydrogen fluoride.

[0052] The yttria stabilized zirconia (YSZ) of orientation which has the magnesia (MgO) of the orientation which has LaAlO3 of ** (100) orientation and the surface layer of ** crystallinity Seria (CeO2) (100), or the surface layer of ** crystallinity Seria as an example of the material which fulfills this condition (100) is mentioned.

[0053] ** As for crystalline Seria of **, adjustment of a grid with the Y123 crystal structure is performed in the direction of a grid and the direction of 45 degrees of surface. Thus, it is not restricted to a lattice spacing being in agreement with lattice matching. Regardless of the direction of an original grid, if the gap between grids is in agreement, it will say that the mutual grid has consistency and will not interfere.

[0054] Spreading of the coating solution to a base material can apply various methods, such as a spin coat which trickles a coating solution into a base material and is made to rotate a base material, and a DIP coat from which a base material is dipped and pulled up in a coating solution. At this time, for example, a spin coat, the thickness of the film of a mixed trifluoroacetic acid metal salt is controllable by adjusting the rotational speed and the rotation acceleration time of a base material.

[0055] In addition, since a solvent will evaporate all over a spin coat if solvents with high vapor pressure, such as a methanol, are used, a special desiccation production process is not needed.

[0056] (8) Heat-treat mixed trifluoroacetic acid metal ****, and create a superconduction precursor (S18).

[0057] This heat treatment installs the base material with which mixed trifluoroacetic acid metal **** was formed in a heat treating furnace, and where the inside of a heat treating furnace is made into a humidification oxygen ambient atmosphere, it is performed.

[0058] Drawing 2 is one showing the time amount in this heat treatment process, and the relation of temperature of a graph.

** The temperature in a heat treating furnace rises from time of day O rapidly from a room temperature to 100 degrees C between ta(s)1 (about 7 minutes after heat treatment initiation). At this time, the inside of a heat treating furnace is placed into the oxygen ambient atmosphere which ordinary pressure dried. In addition, all next heat treatment processes can be performed under ordinary pressure.

[0059] ** When time of day ta1 comes, the ambient atmosphere in a heat treating furnace is changed into the pure oxygen ambient atmosphere of the humidified ordinary pressure. And the temperature in a heat treating furnace (about 17 hours after heat treatment initiation) rises from time of day ta1 from 100 degrees C to 250 degrees C between ta(s)2.

[0060] The pure oxygen ambient atmosphere humidified at this time is set as the range of 4.2 - 12.1% of humidity. For adjusting humidity, it can carry out to Mizuuchi of a predetermined temperature by letting the air bubbles of a controlled atmosphere (oxygen gas) pass. That is, humidity is decided by maximum vapor tension in the air bubbles when passing underwater, and this maximum vapor tension is determined by temperature.

[0061] ** From 250 degrees C to 300 degrees C, the temperature in a furnace rises from time of day ta2

to 400 degrees C after that between ta(s)3 (40-minute about room per hour) between time of day ta3 and ta4 (20-minute about room). It is maintained at the pure oxygen ambient atmosphere which humidified the ambient atmosphere in a heat treating furnace also at this time. As for a heat treating furnace, natural air cooling is performed after time of day ta4. Although the inflow of a controlled atmosphere stops at this time, the oxygen gas humidified as a controlled atmosphere is piling up.
[0062] As a result of the above heat treatment, the trifluoroacetic acid component of a mixed trifluoroacetic acid metal is decomposed, and a superconduction precursor is formed. Specifically, the following reactions arise.
(CF3COO) 3Y -> YF3 or -- YOF(CF3COO)2</SUB> Ba -> BaF3(CF3COO)2Cu -> CuO [0063] Since a trifluoroacetic acid component decomposes as a gas component at this time, a residual into the superconduction precursor of a carbon element is not almost.
[0064] (9) Give heat treatment and oxygen annealing to a superconduction precursor, and create a superconductor (S19).
[0065] By making the controlled atmosphere in the case of heat treatment contain a steam, the fluoride in a superconduction precursor (for example, YF3, or YOF, BaF2, CuO) reacts with moisture as follows, generates hydrogen fluoride, and turns into an oxide.
2YF(s)3 + 3H2O -> Y2O3 + 6HF** (2YOF + H2O -> Y2O3 + 2HF**)
BaF2 + H2O -> BaO + 2HF** [0066] These oxides form Ba2YCu 3O6.5 immediately. Adjustment of the amount of oxygen by oxygen annealing is performed to this oxide Ba2YCu 3O6.5, and Y123 system oxides superconductors of Ba2YCu 3O7 are generated.
[0067] Drawing 3 is one showing the time amount in this heat treatment and an annealing production process, and the relation of temperature of a graph.
** If heat treatment is started, when [this] the temperature up of the inside of a heat treating furnace is carried out from a room temperature, in early stages of a temperature up production process, the dry mixed gas which comes to mix 1000 ppm oxygen gas to inert gas (also the following which does not interfere with nitrogen gas, either the same), such as Ar gas, will be filled in a heat treating furnace (till time of day tb1 (about 4 minutes after heat treatment initiation, temperature of 100 degrees C)).
[0068] Here, this mixed gas does not interfere by ordinary pressure, and the following heat treatments and oxygen annealing of it are the same as that of this point. In addition, it is one example for [1000 ppm / of oxygen densities here / and processing-time] 4 minutes etc., and processing on condition that others is also possible. This point, the following heat treatment processes, etc. are the same.
[0069] ** A controlled atmosphere changes to the inert gas and the confusion gas (4.2 - 12.1% of humidity and 1000 ppm oxygen are mixed) of oxygen which were humidified at time of day tb1. After that, the temperature in a heat treating furnace rises to 775 degrees C, rises at time of day tb2 (about 38 minutes after heat treatment initiation) to 800 degrees C further between time of day tb2-tb3 (10-minute about room), and is kept constant at it by time of day tb3-tb4 (about 1 hour). By humidifying the controlled atmosphere, the moisture used for the decomposition will be supplied to a superconduction precursor.
[0070] ** It changes to the inert gas and the confusion gas (they are mixing and the ordinary pressure about 1000 ppm oxygen) of oxygen gas which the controlled atmosphere dried again at time of day tb4. Then, the inside of a heat treating furnace is kept at 800 degrees C till time of day tb4-tb5 (10-minute about room), and after that, it falls and goes temperature and becomes 525 degrees C slowly at the time of time of day tb6 (3 hours and about 32 minutes after heat treatment initiation).
[0071] Even **-** of a more than is a heat treatment process, a superconduction precursor generates hydrogen fluoride by the reaction with moisture, is disassembled, it becomes an oxide, and Ba2YCu 3O6.5 is immediately formed from these oxides in the meantime.
[0072] ** A controlled atmosphere is changed to the desiccation oxygen gas of ordinary pressure at time of day tb6, and the production process of oxygen annealing is started.
[0073] Between time of day tb6 and tb7 (26-minute about room), temperature falls at the same pace as the between from time of day tb5 to tb6, and it becomes 450 degrees C at time of day tb7.
[0074] From time of day tb7 before tb8 (for 30 minutes), temperature is kept at 450 degrees C and

oxygen annealing advances further. The production process of oxygen annealing is ended at time of day tb8 (4 hours and about 28 minutes after heat treatment initiation), and a heat treating furnace is cooled. In addition, the desiccation oxygen gas ambient atmosphere is maintained also during this cooling.
[0075] (2nd operation gestalt) Drawing 4 is flow drawing showing the manufacture method of the oxides superconductors concerning the 2nd operation gestalt of this invention. Steps S21-S29 shown in this flow drawing correspond with steps S11-S19 of drawing 1 , respectively.
[0076] Also in this operation gestalt, the yttrium is expressed as a thing representing "one or more kinds of metallic elements chosen from the lanthanoids group and the yttrium (Y)." With this operation gestalt, yttrium acetate, barium acetate, and copper acetate are separately dissolved in water by S21, and three kinds of acetic-acid metal salt water solutions A, B, and C are created. Also after that in S22-S25, the trifluoroacetic acid metal salts A, B, and C, the 1st trifluoroacetic acid metal salt A, B, and C, and the 2nd trifluoroacetic acid metal salt A, B, and C are created according to the individual, respectively. And in S26, the 2nd trifluoroacetic acid metal salt A, B, and C is mixed, and the coating solution is created.
[0077] That is, with this operation gestalt, an yttrium, barium, and copper are processed according to an individual to S21-S25, and the point mixed very much to S26 is different from the 1st operation gestalt.
[0078] Thus, even if it mixes just before refining the trifluoroacetic acid yttrium etc. separately and creating a coating solution, creation of oxides superconductors is possible.
[0079] In respect of others, since especially this operation gestalt is not different from the 1st operation gestalt, it omits explanation.
[0080]
[Example] The example of this invention is shown below.
(Example 1) The powder of the hydrate of yttrium acetate (Y(OCOCH3) 3), barium acetate (Ba2 (OCOCH3)), and copper acetate (Cu2 (OCOCH3)) is dissolved in pure water by each mole ratio 1:2:3 (S of drawing 1 it is the same as that of correspondence and the following to 11), the trifluoroacetic acid of a reaction equimolecular amount, mixing, and stirring are performed, and the mole ratio of the ion of Y, Ba, and Cu obtains the mixed trifluoroacetic acid metal salting in liquid of 1:2:3 (S12).
[0081] Putting the obtained mixed trifluoroacetic acid metal salting in liquid into an eggplant mold flask, and decompressing by the rotating evaporator, it distills for 12 hours and translucent blue gel or the 1st sol-like purification mixing trifluoroacetic acid metal salt is obtained (S13).
[0082] The sum total content (it is about 2 - 8 % of the weight to the 1st purification mixing trifluoroacetic acid metal salt) of moisture and an acetic-acid component which constitutes the 1st sol or gel of a purification mixing trifluoroacetic acid metal salt is measured by measuring the weight of the 1st purification mixing trifluoroacetic acid metal salt. and the methanol (replaceable material) which corresponds by 100 times this sum total content by weight -- in addition, the 1st purification mixing trifluoroacetic acid metal salt is dissolved, and a mixed trifluoroacetic acid solution is created (S14). This solution is distilled under reduced pressure in a rotating evaporator for 8 hours, and the 2nd purification mixing trifluoroacetic acid metal salt which consists of translucent blue gel or a translucent blue sol is obtained (S15).
[0083] The 2nd obtained purification mixing trifluoroacetic acid metal salt was dissolved in the methanol as a solvent, and the coating solution of 1.52M (mol/l), 2.34M, and 2.78M was obtained by metal ion conversion, respectively (S16).
[0084] The coating solution of each concentration was used and membranes were formed by crystal orientation applying and drying for acceleration-time 0.4 seconds with a spin coat on the single crystal substrate of LaAlO3 of (100) as a base material on rotational-speed 4000r.p.m. and the conditions for holding-time 120 seconds of rotation (S17).
[0085] On the temperature conditions shown in drawing 2 , it heat-treated in 4.2% of humidification ambient atmosphere, and the superconduction precursor was created (S18).
[0086] Then, heat treatment in the mixed-gas ambient atmosphere of 4.2% humidification which mixed 1000 ppm oxygen to the argon on the temperature conditions of drawing 3 , and oxygen annealing in the inside of a desiccation pure oxygen ambient atmosphere were performed, and the superconductor was created (S19).

[0087] The obtained superconductor is an X diffraction (X-Ray Diffract). Measurement performed identification of the phase of crystal orientation, and analysis of a priority stacking tendency. Moreover, the critical current (Ic) in temperature 77K magnetic field 0T was measured using the direct-current 4 terminal method, the division of this was done with the cross section of a superconductor film, and it asked for critical current density (Jc). The cross section of a superconductor film calculated the whole quantity of a superconductor film by induction joint plasma luminescence (Induced Coupled Plasma) spectroscopy, and it computed it by having done the division of this with the surface area of a superconductor film.
[0088] The measurement result of an X diffraction is shown in drawing 5 , and the measurement result of critical current density is shown in drawing 6 . Here, what created the superconductor without performing steps S14 and S15 of drawing 1 as an example of a comparison was used.
[0089] The horizontal axis of drawing 5 is the graph with which diffraction reinforcement (arbitration unit) was expressed for angle-of-diffraction 2theta at the time of using CuK-alpha rays as an X-ray as an axis of ordinate, an upper case shows an example 1 and the lower berth shows the example of a comparison. It turns out that the example 1 or the example of a comparison also shows the almost same diffraction pattern, and the superconductor crystal structure of Y123 system is formed.
[0090] Drawing 6 is the graph with which the horizontal axis expressed the sum total content of the moisture in the 2nd [before coating solution creation] purification trifluoroacetic acid metal salt, and an acetic-acid component, and the axis of ordinate expressed critical current density (Jc). And x plots [O] the example of a comparison for an example 1 on a graph. All the thickness of the superconductor at this time is arranged with 0.15 micrometers.
[0091] To the example of a comparison being the range whose sum total content of moisture and an acetic-acid component is about 3 - 6 % of the weight, in the example 1, a sum total content is less than 2%, and the thing below .5 % of the weight is also contained. That is, in the manufacturing process of a superconductor which skipped steps S14 and S15 of drawing 1 , the sum total content of moisture and an acetic-acid component cannot be creating less than 2% of purification trifluoroacetic acid metal salt.
[0092] Critical current density shows such a big value that the sum total content of moisture and an acetic-acid component is small. The sum total content is over 1x106 [A/cm2] to being 1x106 [A/cm2] degree in the example of a comparison in which the sum total content of the moisture in a purification trifluoroacetic acid metal salt and an acetic-acid component exceeds 2%, even if critical current density is good in less than 2% of the weight of the example 1. And at less than 0.5 % of the weight, a sum total content exceeds 2x106 [A/cm2], and some which showed the value which approaches 5x106 [A/cm2] have it.
[0093] As mentioned above, in an example 1 and the example of a comparison, although the crystal structure itself hardly changes, critical current density has a difference and it turns out that this is decided by the sum total content of moisture and an acetic-acid component. This serves as an impurity in the crystal structure, when moisture, an acetic-acid component, especially an acetic-acid component form a superconductor, and it is considered to be because for supercurrent to be checked.
[0094] (Example 2) In the example 2, yttrium acetate, barium acetate, and copper acetate were used as starting material like the example 1. And steps S11-S13 were made into the same production process as the 1st example.
[0095] Then, in steps S14 and S15, it refined by changing to a methanol and dissolving the 1st purification mixing trifluoroacetic acid metal salt using ethanol.
[0096] Ethanol 50 to 100 times the weight of the sum total content of the moisture in the 1st purification mixing trifluoroacetic acid metal salt and an acetic-acid component was added at step S14, and, specifically, the purification mixing trifluoroacetic acid metal salt of deed 2nd was obtained [the solution] for distillation under reduced pressure for 10 hours using the rotating evaporator (S15). That distillation time amount is long supports that the vapor pressure of ethanol is lower than a methanol.
[0097] The 2nd obtained purification mixing trifluoroacetic acid metal salt was diluted with the methanol like the 1st example, and the coating solution of 1.52M (mol/l) was created by metal ion conversion (S16).

[0098] Then, the superconductor was created at the almost same production process as the 1st example (S17-S19). Making humidity of a humidification pure oxygen ambient atmosphere in creation of the superconduction precursor of step S18 into 12.1% here, the base material used at step S17, spreading conditions, and heat treatment and the annealing conditions of step S19 presupposed that it is the same as that of an example 1.
[0099] When the critical current density of the superconductor created as mentioned above was measured, the good superconduction property was shown like 3.5 MA/cm2 and an example 1 under the conditions of temperature 77K and magnetic field 0T.
[0100] (Example 3) In the example 3, using the hydrate of acetic-acid samarium, barium acetate, and copper acetate as starting material, this was dissolved in pure water and the metal ion mole ratio of Sm, Ba, and Cu obtained the mixed acetic-acid metal salt water solution of 1:2:3 (S11). Subsequent steps S12-S13 were made into the same production process as the 1st example.
[0101] Then, in steps S14 and S15, it refined by changing to a methanol and dissolving the 1st purification mixing trifluoroacetic acid metal salt, using 1-propanol and 2-propanol respectively.
[0102] The 50 times as much 1-propanol as the sum total content or 2-propanol of the moisture in the 1st purification mixing trifluoroacetic acid metal salt and an acetic-acid component was added, respectively, and, specifically, two kinds of mixed trifluoroacetic acid metal salting in liquid was created (S14). The 2nd purification mixing trifluoroacetic acid metal salt of two kinds of deeds was obtained [the solution] for distillation under reduced pressure for 12 hours using the rotating evaporator, respectively (S15). Here, that distillation time amount is long supports that the vapor pressure of propanol is lower than a methanol and ethanol.
[0103] Two kinds of 2nd obtained purification mixing trifluoroacetic acid metal salt was diluted with the methanol like the 1st example, and the coating solution of 1.50M (mol/l) was created by metal ion conversion (S16).
[0104] Then, the superconductor was created at the almost same production process as the 1st example (S17-S19). The base material used by S17 is used as the magnesia (MgO) of the orientation (100) which grew up the crystal layer of Seria (CeO2) into the surface here. 4.2%, the controlled atmosphere [in / for the humidity of the humidification pure oxygen ambient atmosphere in creation of the superconduction precursor of S18 / creation of the superconductor of S19] was made into the mixed gas (1000 ppm oxygen is mixed to an argon) which made humidity 12.1%, and made the spreading conditions of step S16 the same.
[0105] When the critical current density of two kinds of superconductors created as mentioned above was measured, the value of 1.50 MA/cm2 and 1.14 MA/cm2 was acquired under the conditions of temperature 70K and magnetic field 0T, respectively.
[0106] (Example 4) In the example 4, steps S12-S13 created the 1st purification mixing trifluoroacetic acid metal salt at the almost same production process as the 1st example as starting material using the hydrate of yttrium acetate, barium acetate, and copper acetate like the example 1. However, distillation time amount of step S13 was made how many minutes longer than 14 hours and an example 1.
[0107] Then, in steps S14 and S15, it refined by adding the methanol equivalent to the content of the moisture in the 1st purification mixing trifluoroacetic acid metal salt, and an acetic-acid component 200 times the weight of the sum total, and dissolving the 1st purification mixing trifluoroacetic acid metal salt. Distillation time amount at this time was made into 9 hours.
[0108] The 2nd obtained purification mixing trifluoroacetic acid metal salt was diluted with the methanol like the 1st example, and the coating solution of 2.34M (mol/l) was created by metal ion conversion (S16).
[0109] Then, the superconductor was created at the almost same production process as the 1st example (S17-S19). The base material used by S17 is made into the yttria stabilized zirconia (YSZ) of orientation (100) which grew up the crystal layer of Seria (CeO2) into the surface here. The humidity of the humidification pure oxygen ambient atmosphere in creation of the superconduction precursor of step S18 7.1%, Making into 4.2% humidity of the humidification mixed-gas ambient atmosphere (argon gas which mixed 1000 ppm oxygen gas) in creation of the superconductor of step S19, the spreading

conditions of step S17 presupposed that it is the same as that of an example 1.
[0110] When the critical current density of the superconductor created as mentioned above was measured, the value of 3.6 MA/cm2 was acquired under the conditions of temperature 77K and magnetic field 0T, and the superconduction property which was excellent almost like the example 1 was acquired.
[0111]
[Effect of the Invention] according to [as explained above] this invention -- metal acetate -- as a start raw material -- available -- in addition -- and it becomes possible to offer the method of manufacturing the oxides superconductors which have a high property.

[Translation done.]